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Assessment of Arsenic Losses during Ashing: A Comparison of Two Methods Applied to Atmospheric Particulates

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A comparison was made of over 300 pairs of arsenic results from instrumental neutron activation and flameless atomic absorption analyses of atmospheric particulates collected on glass fiber filters. Atomic absorption analyses involved low temperature ashing of filters at high power levels. No matrix modification chemicals were added to the acid extract which was analyzed. Neutron activation results are on the average 9% higher than those obtained by atomic absorption and the difference is statistically significant. This small difference is probably due to the analytical techniques or acid extraction and not in any important way to losses during low temperature ashing. This conclusion is in sharp contrast to other recently reported situations where low temperature ashing losses in analyzing atmospheric particulate were sizable. Although the atmospheres sampled differed somewhat between these situations the most obvious difference was in the combustibility of the filters used in sampling.

The concern with the arsenic content of atmospheric particulate is complicated by two factors: (1) the collection efficiency of a hi-vol sampler if such is used, and (2) concern that low temperature ashing often employed during multi-element analyses of hi-volume filters would volatilize any arsenic there. Only the second concern will be dealt with here.

Reports of the effects of low temperature ashing on arsenic in various matrices have different and sometimes conflicting results. A very recent report specifically concerned with the analysis of arsenic in atmospheric particulate ends with an unqualified recommendation against the use of low temperature ashing when arsenic is of concern. This recommendation

was a result of an experience of significant losses of arsenic even when low power levels were used in the low temperature asher.¹ These conclusions were further complicated by experience which indicated the need to control matrix effects through the addition of chemicals in order to do adequate flameless atomic absorption analyses for arsenic.²

The purpose of this paper is to report on analyses by two analytical techniques of atmospheric particulate collected on glass fiber hi-volume sampler filters. One portion of each filter was ashed in a low temperature asher at high power levels then acid extracted and subjected to a flameless atomic absorption analysis. Another portion of the same filter without any pretreatment was subjected to neutron bombardment and analyzed by instrumental neutron activation. A comparison of these split sample results yields some insight into the situation.

Experimental

Samples

Glass fiber hi-volume sampler filters were exposed for 24 hr each at several continental sites each of which had a non-ferrous smelter nearby. Exposed filters were returned to the laboratory and stored. When taken for analysis each of these filters was cut twice to prepare two aliquot samples, one of which was analyzed by the atomic absorption and the other by the neutron activation analysis techniques.

Atomic Absorption Procedure

The flameless atomic absorption technique utilized a solution prepared by the routine NASN acid extraction procedure.³ In brief, the extract is prepared by subjecting the filter strip to low temperature ashing at 200 watts for 1 hr, refluxing the ashed strip for 4 hr in mixed hydrochloric and nitric acid, evaporating the acid solution nearly to dryness, and diluting to volume with nitric acid. A 45.2 cm² sample of a hi-vol filter was used for this purpose.

Table I. Comparison of concentrations measured by atomic absorption and neutron activation methods from 313 split high-volume samples.

	Atomic absorption	Neutron activation
Overall mean concentration (ng/m ³) of the 313 samples	138	152
Range of concentrations (ng/m ³)	5* to 1300	3* to 1300
Coefficient of variation for repeating a single analysis by each technique (%)	26.6	18.3
Number of pairs of duplicate results used to estimate coefficient of variation	11	84

* discrimination limits

A Perkin-Elmer Model 403 atomic absorption spectrophotometer fitted with a Model 2000 heated graphite atomizer was used.* A 5 μ l injection of the 4.5 N nitric acid extract was dried for 20 sec at 100°C, charred for 45 sec at 1200°C, and atomized for 7 sec at 2700°C with a nitrogen purge gas auto-interrupt. The arsenic content was calculated by using an electronic signal integration from the 193.7 nm line and a net area. This net area is the difference between the integrated signal of the sample and the integrated signal from the reagent blank injected immediately following the sample.

Straightforward calibration using a commercial atomic absorption standard diluted in 4.5 N nitric acid was utilized. Brief tests indicated that background correction, nickel supplements, and calibration by the method of additions improved nothing for these samples.

Neutron Activation Procedure

Samples of 14.5 cm² taken from each of the exposed hi-vol filters were simply irradiated for 4 hr in a nuclear reactor with a nominal flux of 10¹³ neutrons/cm²/sec. The NBS fly ash (SRM 1633) was used as a calibration standard. A decay of 8 days was allowed before counting to minimize sodium interference. At that time the spectrum collection was by means of a 21% efficient Geli detector with a resolution of 2.2 keV FWHM at 1332 keV and a Nuclear Data 4420 analyzer utilizing 2048 channels of storage. The 559 keV line was observed.

The Discrimination Limit

Ideally, an unexposed portion of each exposed hi-vol filter would be available for determination of the blank value for that specific sample. Since this was not the case here, the discrimination limit was defined as a technique dependent atmospheric concentration above which one could with relative certainty ascribe the net result from any analysis to the atmospheric particulate and below which confusion with a contribution from the filter would be very likely.

This was done by analyzing the reserve stock of the group of filters used in the field. The mean value obtained from this group of blank filters was subtracted from the total arsenic content of any exposed sample to obtain a net arsenic content which is then the best estimate of the arsenic content of the particulate matter on that filter.

A tolerance interval was then defined for this entire lot of filters.⁴ The tolerance interval was computed by multiplying the standard deviation of the results from the sample of blank filters analyzed by 3.3 and dividing by an arbitrary 2500 m³ of air. This value for each technique was taken to be the discrimination limit for this sample of filters for that technique.

* Mention of commercial or trade names does not constitute an endorsement or recommendation for use.

Since a sample of ten filters was available from the stock of filters utilized in the field, the factor 3.3 utilized in this one-sided tolerance interval estimate implies approximately 95% certainty that about 97% of all observations smaller than the calculated limit would be due to the filter and not to the particulate deposited on it. The assumption must, of course, be that the sample of filters was representative (random).

The limit of discrimination estimated for the atomic absorption technique was 5 ng of As/m³ and for the neutron activation procedure 3 ng of As/m³ of air. Arsenic values less than these discrimination limits are reported as below discrimination and are not considered further in any subsequent computations.

Results and Calculations

A few samples were analyzed in duplicate by each technique. That is, two pieces from the same filter were handled separately but analyzed by the same technique. This, of course, permits an estimate of the ability of that technique to repeat a measurement on a given filter. A summary of that information is presented in Table I for each technique.

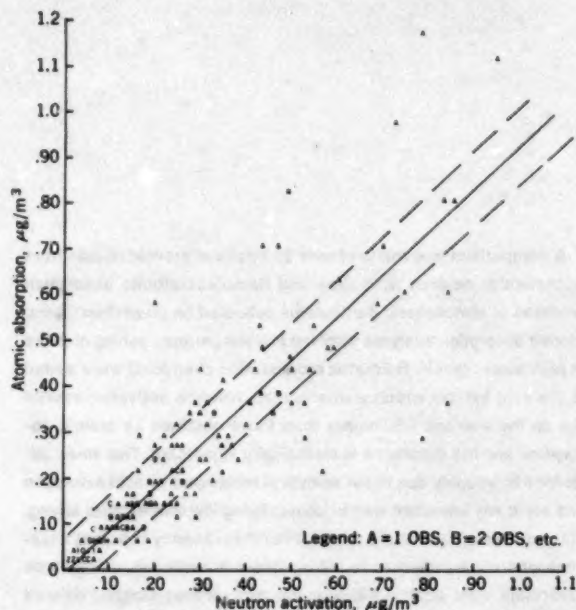


Figure 1. Plot of regression of atomic absorption results on neutron activation results.

The analyses of split samples produced 313 pairs of data where both values were finite—that is, above the respective discrimination limits. A side-by-side computer listing of these data pairs can be obtained from the authors.

Figure 1 presents a plot of the regression of the atomic absorption results upon the neutron activation. The least squares equation is:

$$[\text{atomic absorption}] = -0.00182 + 0.916 [\text{neutron activation}]$$

The intercept is not significantly different from zero but the slope is significantly less than one. This implies that on the whole the neutron activation results are slightly higher than the atomic absorption results.

Another way to present these same data is to compare the distributions of these two identically constituted sample sets. In this way the correlation coefficient can be calculated and an average bias can be computed and then tested for significance. Such summary information is presented in Table II

Table II. Summary statistics from 313 split high-volume samples analyzed by each technique.

Correlation coefficient between techniques	0.92
Percentage mean difference* (%)	-9.2
95% confidence interval for percentage mean difference (%)	-14.8 to -3.6

* Defined as: $AA - NA/NA \times 100$, where AA and NA are overall mean concentration values (138 and 152 ng/m³, Table I) measured by atomic absorption and neutron activation, respectively.

which shows that the bias is statistically significant with 95% confidence with the neutron activation giving on the average a higher result. The correlation between the two techniques is quite good.

Discussion

The bias between these sets of results is clearly a great deal smaller than the average bias of over 30% reported in other circumstances.¹ Both these data and the others do agree, however, in that neutron activation generally gives the higher result.

The need then is to examine the possibilities for signal enhancement in the case of the neutron activation and signal depression in the case of the atomic absorption or loss of As from the particulate in the sample preparation procedure during the atomic absorption only.

The presence of significant quantities of bromine and/or antimony interfere with the determination of As at the 559 keV line. However, a computational test for the presence of the peak is built into the computer algorithm which interprets the gamma ray spectrum. If these interferences are present and the peak cannot be resolved, an upper limit rather than a value for As is printed out. In the overwhelming majority of cases a definite value is produced for As.

The instrument parameters utilized in the atomic absorption were those recommended some time ago by the instrument manufacturer. The charring and atomization temperatures are a bit higher than usual and the very obvious result is that the lifetime of any given tube is severely, though not impractically, limited.

Control of matrix effects by a specific chemical addition was not required in these samples since differences were not observed by calibration by standard additions or the addition of nickel supplements or background correction. This is in rather distinct contrast to other recent reports of quantitations of As in atmospheric particulate.² Although no specific explanation for the lack of need for these measures was sought there was no evidence that any significant suppression of the atomic absorption signal was taking place.

Some credibility is lent to these observations by a comparison with previously reported data. Walsh, *et al.*² performed a low temperature ashing of real atmospheric particulate. When the ashing was completed they split the sample, analyzing a portion by neutron activation and another portion by atomic absorption in order to test analytical techniques only. The data for the 6 paired samples in Walsh, *et al.* Table IV show an average bias of -5% when the computation is done as indicated in the footnote to Table II. That value, if taken to be exact, is indistinguishable from the bias reported here in Table II. However, the confidence interval estimate for the -5% includes zero. In data sets so small quantitative results can be strongly influenced by one unusual but not unreasonable result. In this case that result is sample C₁ the only one in which a higher result was obtained by atomic absorption. If that pair is deleted from the set the mean bias becomes -10.8% with a confidence interval of -19% to -2%. These values are so similar to those in Table II from a very large sample set that the agreement is probably not fortuitous.

These data comparisons do not demonstrate the cause of bias between the two techniques but they do indicate that it is possible at least in some circumstances to do As analyses by flameless atomic absorption without matrix modification and that any bias between the techniques is probably about 10%.

This same data comparison also indicates that As loss during the low temperature ashing on these glass fiber filters is unimportant in spite of the high power levels used. This conclusion is based on the fact that split samples utilized in this work were ashed in the atomic absorption extraction process but nothing was done to them in the neutron activation analysis. In the previously reported work the ashing was done prior to the split of the sample and identical samples were utilized in both techniques. Since the outcomes were indistinguishable in the data comparisons there is no evidence that As was lost in ashing these hi-vol filters.

The experience reported here was, therefore, very different from that reported previously. The composition of the particulate was very likely different in the two situations since here all samples were taken at continental sites and in the previously reported study most of them were apparently taken where marine influences were great. Another and perhaps the most prominent difference between the two studies was that in this work the filter material was noncombustible glass fiber. In the other work the filter material was a combustible cellulose. Perhaps that is the greatest "matrix" effect of all in terms of the processes going on during low temperature ashing for a given kind of matrix.

Conclusion

The work reported here indicates that quantitation of arsenic in atmospheric particulate collected on glass fiber filters at continental sites can be done adequately either by instrumental neutron activation or by flameless atomic absorption spectroscopy with low temperature ashing, acid extraction, and no specific chemical additives. Caution is always important. However, summary dismissal of all arsenic values obtained when low temperature ashing is employed is not defensible.

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